Revision 2

High-Pressure Phase Transition of Fe-bearing Orthopyroxene Revealed by Raman Spectroscopy

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Orthopyroxene is one of the dominant minerals in the Earth’s upper mantle. In this study, we used Raman spectroscopy to investigate the lattice vibration and phase transition of orthopyroxene with four different compositions using diamond anvil cells up to 34 GPa at 300 K. Our orthopyroxene samples contain 0 (En$^{100}$), 9% (En$^{91}$Fs$^{9}$), 11% (En$^{86}$Fs$^{11}$) and 21% (En$^{74}$Fs$^{21}$) Fe respectively. At ambient conditions, we observed that the Raman modes exhibited a negative dependence on the Fe content, with the exception of the modes at ~850 and 930 cm$^{-1}$. In contrast, the two Raman modes increase with increasing the Fe content. The phase transition from metastable α- to β-phase was observed at 12.9-15 GPa for our orthopyroxene samples with less than 21 mol.% Fe, and varying Fe content has a minor effect on the phase transition pressure. Besides of Fe, additional 2-24 mol.% Al can cause phase transition pressure increase from 10-13 GPa to 14-16 GPa. At 29-30.1 GPa, we observed the second apparent change in the Raman spectra for all of our investigated samples. For Fe-bearing orthopyroxene, this change in the Raman spectra and frequency shift is associated with the phase transition from β- to γ-phase, whereas for En$^{100}$, it should be caused by the change of coordination number Si from 4 to 6, or the presence of α-popx phase. Using the obtained Raman frequency shifts, we have also calculated the Grüneisen parameters at high pressures. These parameters are useful for understanding the thermoelastic properties of orthopyroxene at high pressures.

**Keywords:** Raman spectroscopy, orthopyroxene, Fe content, phase transition, high pressure
1. INTRODUCTION

Orthopyroxene, \((\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3\), is a crucial constituent of Earth’s upper mantle (Bernard et al., 2021; Herzberg and Gazel, 2009; Li et al., 2018; Shi et al., 2022; Tollan and Hermann, 2019). According to the pyrolite model, the volume percentage of orthopyroxene is estimated to be 10 vol.% up to 350-km depth (Frost, 2008). Petrological observations suggest that the orthopyroxene content in the subducted harzburgite and lherzolite layer can be as high as 22 vol.% (Bodinier and Godard, 2003; Ringwood, 1975; Ringwood and Irfune, 1988). Although mantle orthopyroxene typically contains 6 mol.% Fe, some diamond inclusions originated from 100-500 km depth have shown that the Fe content in peridotitic orthopyroxene could vary from 3 and 19 mol.% (Stachel and Harris, 2008). In some high-pressure metamorphic rocks, the Fe content in orthopyroxene exhibits a higher compositional range between 50 and 100 mol.% (Brothers and Yokoyama, 1990; Davidson, 1968; Jaffe et al., 1978; White et al., 2001). Therefore, investigating the physical properties of orthopyroxene with varying compositions under relevant pressure and temperature conditions in the Earth's mantle is crucial for understanding the structure and composition of the Earth's deep interior.

Along the normal mantle geotherm, the orthorhombic orthopyroxene (\(\text{Pbca} \) space group, \(\alpha\)-phase) transforms to high-pressure clinopyroxene (\(C2/c\) space group) at \(~8\) GPa and then gradually dissolve into garnet at deeper depth (Akashi et al., 2009; Kung et al., 2005). However, the path of phase transition in orthopyroxene at high pressures heavily relies on the temperature and composition (Akashi et al., 2009). The transition of orthopyroxene to high-pressure clinopyroxene will be inhibited when temperatures are significantly lower than the normal mantle geotherm (Nishi et al., 2013; Van Mierlo et al., 2013). For example, the \(\alpha\)-MgSiO\(_3\)
orthopyroxene (En$_{100}$) remains metastable and then transforms into its β-phase with a monoclinic structure ($P2_1/c$ space group) at 10.5-13.3 GPa (Kung et al., 2004; Lin, 2004; Xu et al., 2018), which can be preserved to ~40 GPa (Serghiou et al., 2000). Both α- and β-phase can remain metastable up to 800 K at 520-km depth (Xu et al., 2020). Previous studies also investigated the influence of Fe on the phase transition of orthopyroxene (Xu et al., 2020). For orthopyroxene with 9 mol.% Fe (En$_{91}$Fs$_{9}$), the transition pressure from α- to β-phase is 12.3 GPa at 300 K, which is similar to the Mg-endmember. However, Fe-bearing β-phase further transforms into the γ-phase ($Pbca$ Space group) at 28.4 GPa (Finkelstein et al., 2015). Increasing the Fe content from 30 to 82 mol.% only can weakly decrease the α-β phase transition pressure to 11 GPa and lower the β-γ phase transition pressure to 12 GPa (Dera et al., 2013; Xu et al., 2020). But for pure Fe endmember (Fs$_{100}$), orthopyroxene transforms into a different monoclinic β-phase with space group $C2/c$ at ~6 GPa and then γ-phase at ~13 GPa (HughJones et al., 1996; Xu et al., 2020). Experimental constraints on the transition from β- to γ-phase for orthopyroxene with less than 20 mol.% Fe are still lacking.

Here, we have performed high-pressure Raman measurements to well constrain the phase transition of orthopyroxene in four different compositions with varying Fe content in symmetric diamond anvil cells (DACs) up to 34 GPa and 300 K. Results from Raman measurements can also be used to identify orthopyroxenes as geological marker (Borromeo et al., 2022). The collected Raman spectra were used to determine the influence of Fe content on the variation of the vibration modes and help to identify the occurrence of the phase transition. Together with previous thermal equation of state, we have calculated thermal Grüneisen parameters of
metastable phases at high pressures which are of great importance to calculate the thermal and elastic properties of orthopyroxene.

2. EXPERIMENTAL DETAILS

Four orthopyroxene single-crystal samples were used in this study. Composition of these four samples were analyzed using electron microprobe in the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). The analysis yielded compositions of $\text{MgSiO}_3$ (En$_{100}$), $\text{Mg}_{0.91}\text{Fe}_{0.09}\text{SiO}_3$ (En$_{91}$Fs$_{9}$), $\text{Mg}_{0.86}\text{Fe}_{0.11}\text{Al}_{0.02}\text{Ca}_{0.01}\text{SiO}_3$ (En$_{86}$Fs$_{11}$) and $\text{Mg}_{0.735}\text{Fe}_{0.21}\text{Al}_{0.07}\text{SiO}_3$ (En$_{74}$Fs$_{21}$). En$_{100}$, En$_{91}$Fs$_{9}$ and En$_{86}$Fs$_{11}$ are single crystals from Yangon, Myanmar. En$_{74}$Fs$_{21}$ was purchased from Alfa Aesar Corp. Every sample was cut into random orientation with ~25 $\mu$m in diameter and double-side polished to ~25 $\mu$m in thickness. Rhenium was used as gasket, and the gasket hole was drilled to 235 $\mu$m in diameter. Two ruby spheres were loaded into the sample chamber as the pressure calibrant, and argon was used as the pressure medium for high pressure experiments (Dewaele et al., 2004).

In-situ single-crystal Raman measurements were performed using symmetric DACs equipped with a pair of 400-$\mu$m culet diamonds at the High-Pressure Mineral Physics Laboratory, USTC. An Olympus flat field achromatic objective lens was employed for the collection of Raman spectra with a 532-nm wavelength. The Raman spectra were measured in a backscattering geometry in a confocal configuration. The Raman spectra at ambient conditions were determined for all samples outside DACs. At high pressures, we have performed two runs of Raman
measurements on the intermediate composition including En$_{01}$Fs$_9$, En$_{86}$Fs$_{11}$ and En$_{74}$Fs$_{21}$. The pure Mg-endmember orthopyroxene was carried out in one run.

3. RESULTS

At ambient conditions, 19 to 23 modes were observed for all the investigated orthopyroxene samples. Typical Raman spectra of orthopyroxene with different Fe contents are shown in Figure 1. The frequencies of Raman-active modes for our four investigated samples at ambient conditions are shown in Figure 2 and Tables 1-4. The measured frequencies for these orthopyroxene samples are in good relevance with the Fe content. Most frequencies have shown negative linear dependence on the Fe content. The Raman mode at $\sim$400 cm$^{-1}$ for En$_{100}$ shows a similar linear decrease with Fe content up to 50 mol.% but exhibits a much stronger reduction by further increasing the Fe content to 100 mol.% In addition, we noted that there were two Raman modes around $\sim$900 cm$^{-1}$ increase with Fe content.

Based on the ambient conditions results, high-pressure Raman spectra for four samples were collected up to 34 GPa at 300 K. For En$_{100}$, all the frequencies followed a nearly linear increase with pressure up to 13.5 GPa. In exceed of 13.5 GPa, we observed the disappearance of modes at $\sim$425, $\sim$560 and $\sim$590 cm$^{-1}$ accompanied with new modes at $\sim$400, $\sim$500 and $\sim$855 cm$^{-1}$. Similar change in the Raman spectra and mode frequencies occur at 12.9 GPa for En$_{01}$Fs$_9$, 15 GPa for En$_{86}$Fs$_{11}$ and En$_{74}$Fs$_{21}$ (Figures 4-6). Another obvious change in Raman spectra was noted to occur at approximately 30 GPa for all the investigated orthopyroxene, characterized by the variation in the pressure dependence of Raman frequencies.
4. DISCUSSION

4.1. Raman modes at ambient conditions

The obtained results were first used to understand the influence of Fe on the Raman frequency of orthopyroxene at ambient conditions. Our Raman spectra of orthopyroxene are similar to previous studies (Chopelas, 1999; Huang et al., 2000). Meaning of each Raman mode for orthopyroxene has been well interpreted by Stangarone et al. (2016). The variation of the Raman modes with Fe content are relevant to the vibrational frequency, $\nu$, of a simple harmonic oscillator (Huang et al., 2000; Stangarone et al., 2016), which can be expressed as:

$$\nu = -\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where $\mu$ is the reduced mass, $k$ is the force constant which is assumed to be an inverse function of interatomic distance. Addition of Fe increases the reduced mass, $u$, and bond length of orthopyroxene which explains the negative correlation of most Raman modes with Fe substitution. When the Fe content in orthopyroxene is less than 50 mol.%, the Raman mode at $\sim$400 cm$^{-1}$ exhibits a similar trend with pressure to most other modes. Yet further elevating the Fe content above 50 mol.% in orthopyroxene produces an enhanced reduction in the mode frequencies. This may be due to different substitution mechanism in orthopyroxene by varying the Fe content. Fe primarily occupies the M2 sites when the Fe content in orthopyroxene is less than 50 mol.%, whereas it starts to substitute Mg in the M1 sites when the abundance is greater than 50% (Domeneghetti et al., 1995; Domeneghetti et al., 1985; Proyer et al., 2004; Stangarone et al., 2016; Stangarone et al., 2023). The correlation of Raman frequency with Fe content is thus mainly related to the variation of atomic mass, volume and bond length caused by Fe substitutes for Mg.
4.2. Phase transition of orthopyroxene

We have also plotted the wavenumber of β- and γ-phase as function of Fe content at 16 and 30 GPa, respectively (Figures S1-S2 in the supplemental material). The Raman shifts of the β- and γ-phase generally exhibit a negative correlation with Fe substitution, similar to the α-phase. Specifically, around ~1000 cm\(^{-1}\), the Raman mode for the β-phase increases with Fe content. The phase transition in orthopyroxene at 300 K was determined by the frequency discontinuities and change in the pressure dependence of some modes at high pressures (Figures 3-6). We identify the α- to β-phase transition to occur at 13.5 GPa for En\(_{100}\), 12.9 GPa for En\(_{91}\)Fs\(_{9}\), 15 GPa for En\(_{86}\)Fs\(_{11}\), and 15 GPa for En\(_{74}\)Fs\(_{21}\) (Figure 7). Together with previous experimental results, our experimental results have shown that the α-β phase transition pressure for Al-free orthopyroxene with varying Fe content is lower than the corresponding Al-bearing phase. Transition from the α- to β-phase for Al-free orthopyroxene with less than 60 mol.% Fe occurs between 10 and 13 GPa (Dera et al., 2013; Finkelstein et al., 2015; Lin, 2004; Xu et al., 2020; Xu et al., 2018; Zhang et al., 2013a; Zhang et al., 2013b). Further elevating the Fe content above 60% leads to a dramatic decrease in the phase transition pressure (Dera et al., 2013; Xu et al., 2020). Addition of Al leads to an increase in the α- to β-phase transition pressure. Orthopyroxene with 2-24 mol.% Al has a phase transition to occur at 14-16 GPa (Xu et al., 2022; Zhang et al., 2013b). In contrast, En\(_{91}\)Fs\(_{9}\) contained virtually no other trace elements, consistent with previous research results. The phase boundary of the En\(_{100}\) sample was found to be higher than those reported in previous studies, primarily due to the large pressure intervals used in earlier experiments (Lin, 2004; Xu et al., 2020; Xu et al., 2018; Zhang et al., 2013b).
The change in the pressure dependence of Raman modes at ~29 GPa for all of our orthopyroxene samples except En100 is related to the β- to γ-phase transition (Figure 7). We observed that in En100, the Raman frequencies at around ~650 and ~1100 cm\(^{-1}\) have merged into a single mode, each comprising three peaks. All the Raman modes above 31 GPa exhibit different pressure dependence compared to modes between 14 and 30 GPa. This change in the Raman modes could be related to the coordination number change of Si from 4 to 6 or the transition to α-popx phase which have been reported by two previous experimental studies (Finkelstein et al., 2015; Serghiou et al., 2000). Our experimental results indicate that the transition pressure from β- to γ-phase are nearly independent of Fe when the Fe content in orthopyroxene is less than 60 mol.%. Further increasing Fe content up to 82 mol.% leads to a substantial decrease in the phase transition pressure (Dera et al., 2013; Xu et al., 2020). Once the Fe content in orthopyroxene is above 80 mol.%, addition of Fe has minimum effect on the phase transition pressure to the γ-phase. As a result, β-phase exists in a much narrow pressure range for orthopyroxene with 82-100 mol.% than the corresponding phase with less than 82 mol.% Fe.

4.3. Grüneisen parameters

The obtained Raman frequency shifts allow us to derive the isothermal Grüneisen parameters at high pressures. The isothermal Grüneisen parameter can be calculated as follows:

\[
\gamma_i = -\frac{\partial \ln \nu_i}{\partial \ln V} = \frac{V_i}{\nu_i} \frac{d\nu_i}{dV} = \frac{K_T}{\nu_i} \frac{d\nu_i}{dP} \tag{2}
\]

where \(\nu_i\) is the \(i\)th mode of the lattice vibration, \(V\) is the unit-cell volume, and \(K_T\) is the isothermal bulk modulus at a given pressure. The values of \(\nu\) and \(d\nu/dP\) were derived by fitting the experimental data using a polynomial function in this study. The influence of Fe on the bulk modulus of α-orthopyroxene at ambient conditions, \(K_{T0}\), was summarized in Figure 8 using
previous experimental results (Dera et al., 2013; Hovis et al., 2021; Hugh-Jones and Angel, 1997; Jackson et al., 2003; Nestola et al., 2008; Xu et al., 2020; Xu et al., 2022; Xu et al., 2018; Zhang et al., 2013a; Zhao et al., 1995). There is a strong trade-off between the bulk modulus $K_{T0}$ and its pressure derivative, $K'$ determined from the X ray diffraction study. For α-orthopyroxene, the value of $K'$ is greater than general mantle minerals with values ranging between 7.5 and 8.5. Here, we used an average $K'$ of 8 and re-analyzed previous experimental results to constrain $K_{T0}$ and obtained (Figure 8):

$$K_{T0} (\alpha\text{-phase}) = -0.05X_{Fe} + 109.80$$

Experimental constraints on the equation of state and elastic properties of both β- and γ-phase are limited (Xu et al., 2020; Xu et al., 2022; Xu et al., 2018). We used fixed $K'=4$ to derive $K_{T0}$, and the effect of Fe on $K_{T0}$ is (Figure 8):

$$K_{T0} (\beta\text{-phase}) = 0.81X_{Fe} + 139.71$$

$$K_{T0} (\gamma\text{-phase}) = -0.01X_{Fe} + 131.71$$

Grüneisen parameters, $\gamma$, at high pressures for each Raman mode was calculated and shown in Table S5 in the supplemental material. In general, there is not a very clear correlation between changes in Fe content and the $\gamma$ value (Figure 9). In the α-phase, an increase in Fe content to 11% leads to a decrease in $\gamma$ for mode $v_{10}$. Among the compositions, En$_{91}$Fs$_{9}$ exhibits a lower $\gamma$ value than the other three in the β-phase. In the γ-phase, there is no discernible trend in the $\gamma$ value with varying Fe content. For mode $v_{24}$ and $v_{32}$ in the α-phase, variations in Fe content have a negligible influence on $\gamma$, considering calculation uncertainties. However, in both the β and γ-phases, the relationship between changes in Fe content and the Grüneisen parameter remains unclear.
Orthopyroxene is an important mineral component of the mantle, but the β- and γ-phases of metastable orthopyroxene that exist above 10 GPa can only be present in the cold subduction zone harzburgite and lherzolite layers with temperatures 700-1000 K lower than the normal mantle (Finkelstein et al., 2015; Ganguly et al., 2009). The significance of our study lies in the detailed characterization of the effect of Fe content changes on the structural phase transition of metastable orthopyroxene and the influence of the transitions on the Grüneisen parameter, which can be directly applied to understand the effects of compositional changes on the sound velocity and density structure of cold harzburgite and lherzolite layers in the subduction slab. Combined with previous high-pressure research results, we observed that the effect of Fe content changes from 0-80% on the α- to β-phase transition pressure of orthopyroxene is small, and the transition mainly occurs from the bottom of the upper mantle to the top of the transition zone. For instance, the α- to β-phase transition for orthopyroxene with 11% Fe has a small effect on the longitudinal and transverse wave velocities, less than 2%, and a density change of about 2% (Li et al., 2022). Additionally, the transition from metastable β-orthopyroxene to γ-phase occurs at pressures exceeding 29 GPa. Therefore, the possibility of metastable γ-phase for orthopyroxene with less than 20% Fe existing in the mantle is small from the 300-K experimental results. However, the Clapeyron slope of the β-γ phase boundary remains unknown. Further high pressures and temperatures experimental research is thus needed which is crucial for our understanding of the density and sound velocity structure of subduction slabs in response to compositional changes.
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**FIGURE 1.** Typical Raman spectra of orthopyroxene at high pressures and 300 K. (a) En_{100}; (b) En_{91}Fs_{9}; (c) En_{86}Fs_{11}; (d) En_{74}Fs_{21}. Blue ticks: Raman modes of \( \alpha \)-orthopyroxene; red ticks: Raman modes of \( \beta \)-orthopyroxene; orange ticks: Raman modes of \( \gamma \)-orthopyroxene.

**FIGURE 2.** Raman shifts of orthopyroxene with different Fe content at ambient conditions. Solid circles: this study; open circles: previous experimental results (Chopelas, 1999; Huang et al., 2000). Red lines: fitting results.
FIGURE 3. Raman shifts of En$_{100}$ at high pressures and 300 K. Blue: α-orthopyroxene; red: β-orthopyroxene; orange: γ-orthopyroxene.

FIGURE 4. Raman shifts of En$_{91}$Fs$_{9}$ at high pressures and 300 K. Blue: α-orthopyroxene; red: β-orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different experimental runs.

FIGURE 5. Raman shifts of En$_{86}$Fs$_{11}$ at high pressures and 300 K. Blue: α-orthopyroxene; red: β-orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different experimental runs.

FIGURE 6. Raman shifts of En$_{74}$Fs$_{21}$ at high pressures and 300 K. Blue: α-orthopyroxene; red: β-orthopyroxene; orange: γ-orthopyroxene; circles and diamonds represent different experimental runs.

FIGURE 7. Phase diagram of orthopyroxene at high pressures. Red: this study; green: (Lin, 2004); pink: (Zhang et al., 2013b); gray: (Zhang et al., 2013a); yellow: (Dera et al., 2013); purple: (Finkelstein et al., 2015); blue: (Xu et al., 2018); orange: (Xu et al., 2020); black: (Xu et al., 2022); circle: Fe-bearing orthopyroxene; diamond: Fe- and Al-bearing orthopyroxene; solid lines: phase boundary for the Al-free orthopyroxene; dash line: phase boundary for the Al-bearing orthopyroxene. The subscript in Al on the figure shows the Al content in orthopyroxene: Al/(Mg+Fe+Al).

FIGURE 8. Unit cell volume ($V_0$) and isothermal bulk modulus ($K_{T0}$) of orthopyroxene at ambient conditions. (a) $V_0$ for α-orthopyroxene; (b) $V_0$ for β-orthopyroxene; (c) $V_0$ for γ-orthopyroxene; (d) $K_{T0}$ for α-orthopyroxene; (e) $K_{T0}$ for β-orthopyroxene; (f) $K_{T0}$ for γ-orthopyroxene. We reanalyzed the pressure-volume data in literature with fixed $K_{T0}' = 8$ for α-orthopyroxene (Dera et al., 2013; Hovis et al., 2021; Hugh - Jones and Angel, 1997; Nestola et al., 2008; Xu et al., 2020; Xu et al., 2022; Xu et al., 2018; Zhang et al., 2013a). For both β- and γ-phase, with fixed $K_{T0}' = 4$, $V_0$ and $K_{T0}$ are from previous experimental studies (Xu et al., 2020; Xu et al., 2022; Xu et al., 2018).
FIGURE 9. Grüneisen parameter of orthopyroxene at high pressures. (a) $v_1$; (b) $v_{10}$; (c) $v_{24}$; (d) $v_{32}$. Blue: En$_{100}$; red: En$_{91}$Fs$_9$; orange: En$_{86}$Fs$_{11}$; black: En$_{74}$Fs$_{21}$. The data are calculated using the single experimental Raman-active mode in this study together with data summarized in Figure 8, Table S5. Calculated uncertainties are shown as vertical ticks on the bottom left.
TABLE 1. Regression constants of En100 for Raman modes determined in $\Delta \nu = \nu_0 + aP$ at high pressures and 300 K.

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<th>$\nu_0$</th>
<th>$a$</th>
<th>$R^2$</th>
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TABLE 2. Regression constants of En$_{91}$Fs$_{9}$ for Raman modes determined in $\Delta v = v_0 + aP$ at high pressures and 300 K.

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$\nu$, $\nu_0$, and $\Delta \nu$ are in cm$^{-1}$, $P$ in GPa, and the constant, $a$ has the corresponding units. $\nu_i$ is the frequency measured at ambient conditions. $R^2$ is the correlation coefficient.
TABLE 3. Regression constants of $\text{En}_{66}\text{Fs}_{11}$ for Raman modes determined in $\Delta \nu = \nu_0 + aP$ at high pressures and 300 K.

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$v_i$, $\nu_0$, and $\Delta \nu$ are in cm$^{-1}$, $P$ in GPa, and the constant, $a$ has the corresponding units. $\nu_i$ is the frequency measured at ambient conditions. $R^2$ is the correlation coefficient.
### TABLE 4. Regression constants of En$_{34}$Fs$_{21}$ for Raman modes determined in $\Delta v = v_0 + aP$ at high pressures and 300 K.

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<td>346.5</td>
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<td>$v_7$</td>
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<td>4.16</td>
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</table>

$v_i$, $v_0$, and $\Delta v$ are in cm$^{-1}$, $P$ in GPa, and the constant, $a$ has the corresponding units. $v_i$ is the frequency measured at ambient conditions. $R^2$ is the correlation coefficient.
Fig 1
Fig 2
\[ \alpha\text{-opx} \quad \beta\text{-opx} \]

a) \[ \text{En}_{100} \]

b) \[ \text{Pressure (GPa)} \]

Fig 3
Fig 4
Ramanshift (cm$^{-1}$) vs Pressure (GPa)

Fig 5
Fig 6

Raman Shift (cm\(^{-1}\)) vs. Pressure (GPa) for different phases of opx (α-opx, β-opx, γ-opx).

- **a** En\(_{74}\)Fs\(_{21}\)
- **b** En\(_{76}\)Fs\(_{21}\)

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Fig 7
Fig 8
Fig 9

Grüneisen parameter vs Pressure (GPa)

- a. $\nu_1$
- b. $\nu_{10}$
- c. $\nu_{24}$
- d. $\nu_{32}$